

## HETEROGENEOUS PHOTOCATALYSIS OF SULFONAMIDES USING TiO<sub>2</sub> AND ZnO PHOTOCATALYSTS WITH MERCURY-VAPOR AND LED LIGHT SOURCES

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### Abstract

Sulfonamides are one of the most often used antibiotics worldwide. The spread of antibiotic-resistant bacteria and the serious health problems caused by them justify the importance of removing antibiotics and their metabolites from water. Heterogeneous photocatalysis is one of the promising methods for elimination of trace organic pollutants from water. This work aims at the investigation of heterogeneous photocatalytic removal of two sulfonamide antibiotics, sulfamethazine and sulfamethoxypyridazine. Commercially available TiO<sub>2</sub> and ZnO were used as photocatalysts, and a mercury vapor lamp (300-400 nm) and UV-LEDs (398 nm) were used as light sources. The efficiency and cost-effectiveness of heterogeneous photocatalysis in the removal of sulfonamides were compared, using TiO<sub>2</sub> and ZnO, in suspensions irradiated with mercury vapor lamp and LEDs. The mercury vapor lamp was found to be more effective due to the better utilization of UV light by the photocatalysts. The LED light source was also worse in terms of operating costs, and TiO<sub>2</sub> with mercury vapor lamps was the most efficient at removing the total organic carbon content.

### Introduction

Countless recalcitrant organic pollutants, like pesticides and pharmaceuticals have been detected in the wastewater, and in natural waters worldwide [1]. The water pollution caused by different antibiotics is especially alarming, since they are responsible for the emergence of antibiotic-resistant bacteria. Sulfonamides are a family of antibiotics that are widely used in both veterinary medicine and human healthcare. Some of them are endocrine disrupting, and highly resistant to biological degradation [2, 3].

Advanced Oxidation Processes (AOPs) have been investigated for a long time to remove organic pollutants, which cannot be eliminated via conventional biological water treatment processes. Probably the most researched method is heterogeneous photocatalysis. When a semiconductor is irradiated with photons, having energy higher than the band gap of the catalyst, photogenerated charge separation occurs. The formed conduction band electron ( $e_{cb}^-$ ) and valence band hole ( $h_{vb}^+$ ) may react with the organic pollutants, or with O<sub>2</sub> and H<sub>2</sub>O, resulting in the formation of other reactive species. Hydroxyl radicals (HO•) are the most important due to their high reactivity and low selectivity.

TiO<sub>2</sub> and ZnO are well-known and widely investigated photocatalysts, due to their efficiency, stability, low price and negligible toxicity. Their band gaps energy are similar; 3.2 eV for TiO<sub>2</sub> and 3.1 eV for ZnO, therefore UV radiation (<400 nm) is required to generate charge separation [4]. Most often a mercury-vapor lamp (MV lamp), emitting in the 300-400 nm range, is applied for excitation of these photocatalysts. Nowadays, due to their intensive development and several advantageous properties, there has been an increased interest in the application of LED light sources in the field of water treatment, even in the case of processes which require UV radiation. [5, 6].

The goal of this study was to investigate the removal efficiency of two sulfonamide antibiotics, sulfamethazine (SMT) and sulfamethoxypyridazine (SMP), using TiO<sub>2</sub> and ZnO photocatalysts under mercury-vapor lamp and commercial UV-LEDs as light sources. The

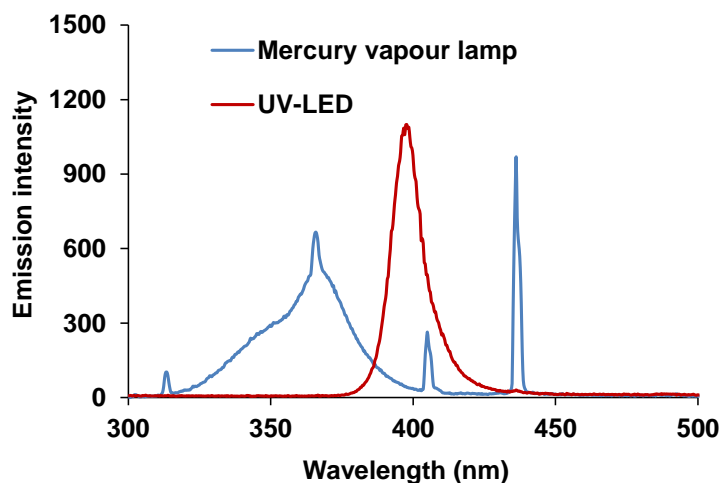
comparison was based on the initial transformation and mineralization rates. The comparison was also made on the basis of the electrical energy required to operate the light sources (cost efficiency) and on the basis of the photon flux emitted by them (photon efficiency).

### Experimental

During the photocatalytic experiments, two reactors were used. In the case of LED light sources, 100 cm<sup>3</sup> suspension was irradiated in a cylindrical glass reactor (volume: 100 cm<sup>3</sup>, inner diameter: 45 mm). As light source, UV (LEDmaster, 288 lumen, 4.6 W;  $\lambda = 398(\pm 15)$  nm) LED tape was used, its length was 1 meter, which contains 60 LED pieces. The reactor was equipped with a water cooling system. The LED tape was fixed on the inner wall of the cooling jacket, which was made from an aluminum tube, having 66 mm inner diameter.

Photocatalytic experiments with MV lamp (GCL303T5/UVA, LightTech, 15 W), were performed in a cylindrical glass reactor (56 mm inner diameter). The volume of the irradiated suspension was 500 cm<sup>3</sup>. The lamp (20.5 mm diameter and 305 mm length) was immersed into the suspension.

The photon flux of both light sources were determined by ferrioxalate actinometry [7] and found to be  $4.83 \times 10^{-6}$  mol<sub>photon</sub> s<sup>-1</sup> for MV lamp and  $1.02 \times 10^{-6}$  mol<sub>photon</sub> s<sup>-1</sup> for UV-LEDs. The emission spectra are shown on Fig. 1.



**Figure 1.** The emission spectra of the light sources

TiO<sub>2</sub> Aeroxide P25 (Acros Organics) and ZnO (Sigma Aldrich) nanoparticles were added to the solutions of sulfonamides, and suspended via ultrasound exposure. The concentration of photocatalysts was 1.0 g dm<sup>-3</sup>, while the concentration of sulfonamides was  $1.0 \times 10^{-4}$  M in each case. The suspensions were saturated with synthetic air for 15 minutes in the dark, then the photocatalytic experiments were started with switching on the light sources.

Before analysis, samples were centrifuged at 15000 RPM, and filtered using 0.22  $\mu$ m syringe filters (FilterBio PVDF-L). The concentration of SMT and SMP was measured by HPLC (Agilent 1100 HPLC device, equipped with DAD detector). Licrosphere 100 RP-18 column was used. The eluent contained 30 % methanol and 70 % formic acid solution (0.10 %), the flow rate was 1.0 ml min<sup>-1</sup>. The detection wavelength was 266 nm for SMT, and 261 nm for SMP. The Total Organic Carbon (TOC) content was measured by Analytik Jena N/C 3100 device.

## Results and discussion

Adsorption plays a crucial role in heterogeneous photocatalysis. Thus, the adsorption of both sulfonamides (SMT and SMP) was determined and found to be negligible in each case. (< 1.0 %). The optima of the catalysts loads were determined in the case of both light sources. The linear part of the kinetic curve (until 15 % conversion) was used to determine the initial transformation rate of sulfonamides. Over  $0.5 \text{ g dm}^{-3}$  catalyst load, no significant increase in the reaction rates was observed, therefore  $1.0 \text{ g dm}^{-3}$  catalyst load was used in the further experiments. The role of direct photolysis of both SMT and SMP was determined without photocatalyst. The transformation rate was found to be much slower in the case of MV lamp and negligible in the case of LEDs, comparing to the transformation rates determined in the presence of photocatalyst (Table 1).

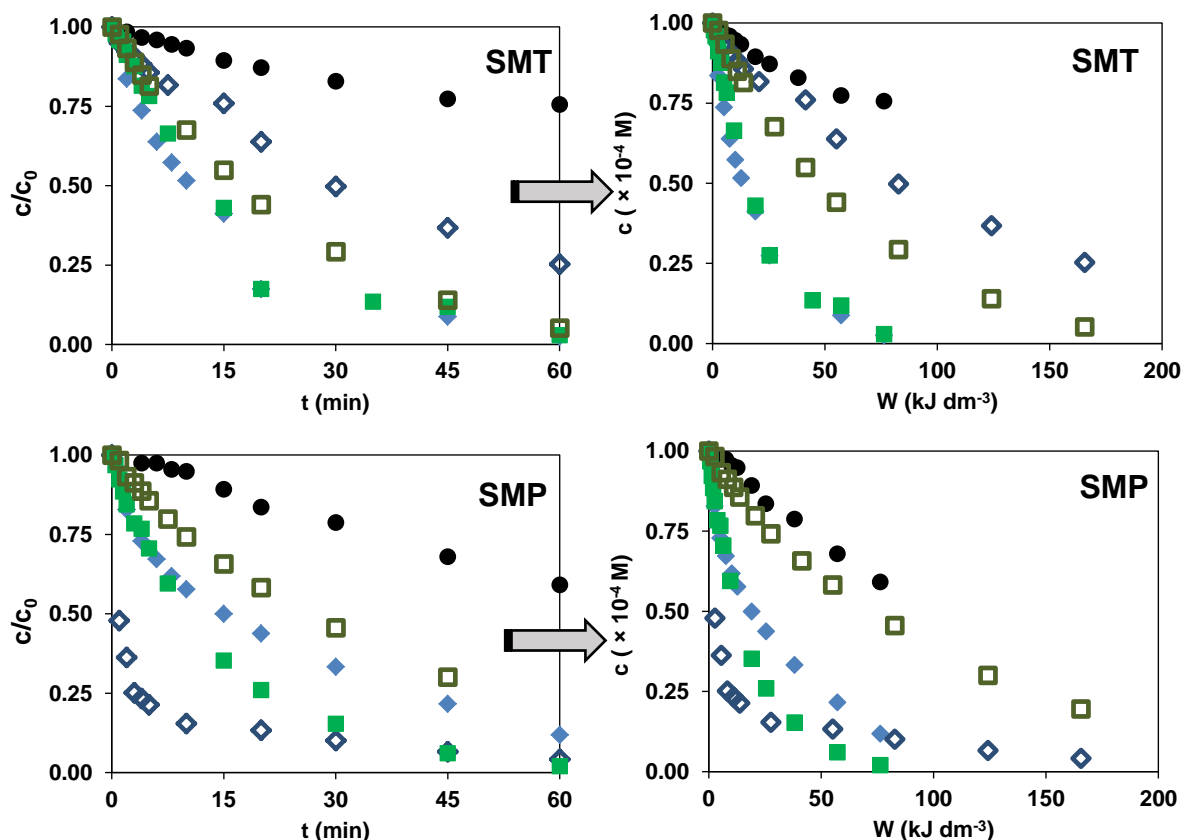
**Table 1.** Initial transformation rate and apparent quantum yield of the transformation

	$r_0 \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$		apparent quantum yield	
	SMT	SMP	SMT	SMP
MVL	$1.18 \times 10^{-8}$	$1.24 \times 10^{-8}$	0.0012	0.0013
<b>TiO<sub>2</sub>/LED</b>	<b><math>5.07 \times 10^{-8}</math></b>	<b><math>8.69 \times 10^{-7}</math></b>	<b>0.0050</b>	<b><u>0.0852</u></b>
<b>ZnO/LED</b>	<b><math>6.13 \times 10^{-8}</math></b>	<b><math>4.80 \times 10^{-8}</math></b>	<b>0.0060</b>	<b>0.0047</b>
<b>TiO<sub>2</sub>/MVL</b>	<b><math>1.16 \times 10^{-7}</math></b>	<b><math>1.49 \times 10^{-7}</math></b>	<b>0.0120</b>	<b>0.0154</b>
<b>ZnO/MVL</b>	<b><math>1.27 \times 10^{-7}</math></b>	<b><math>1.13 \times 10^{-7}</math></b>	<b>0.0130</b>	<b>0.0117</b>

The apparent quantum yields were significantly lower in the case of LEDs emitting at 398 nm than in the case of MV lamp, emitting 300-400 nm light. Its reason is the less effective utilization of photons with lower energy by TiO<sub>2</sub> and ZnO. There was no significant difference between the quantum yields determined for ZnO and TiO<sub>2</sub>, except when TiO<sub>2</sub> and LEDs were used to eliminate SMP, which was extremely fast (Table 1).

The comparison was also performed on the basis of the electrical energy consumption to treat a unit volume ( $1.0 \text{ dm}^3$ ) suspension, which was calculated using the electrical power of the light sources (4.6 W for LEDs and 15 W for MV lamp). The electrical energy, required for the transformation is much higher in the case of LEDs than in the case of MV lamp, except for SMP, using TiO<sub>2</sub>.

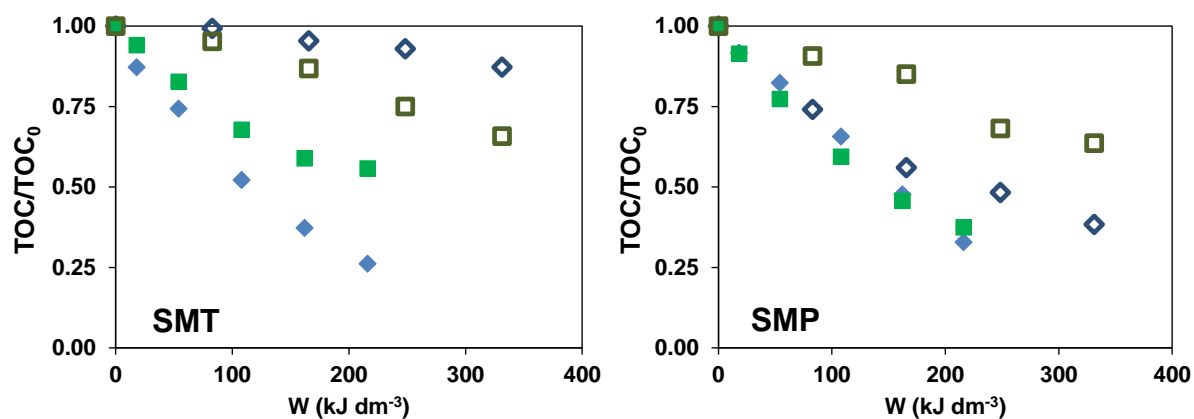
The mineralization (complete transformation to CO<sub>2</sub>, H<sub>2</sub>O, and inorganic ions) of the organic content is also important during water treatment, as the degradation products may also have a similar, or even higher biological effect than the parent compound. Due to the high stability of TiO<sub>2</sub> and the high HO• formation rate, the TOC was reduced by 75% after 120 minutes. ZnO was less effective in the mineralization, despite the similar initial reaction rates, as only 44% TOC content was removed after 120 minutes. In the case of LEDs, only 13% TOC content was removed in TiO<sub>2</sub> containing suspension, while in ZnO containing suspension the decrease was 34%.



**Figure 2.** The relative concentration vs. the time of treatment and concentration vs. the electrical power input per volume

●: MV lamp (no photocatalyst); ◆: TiO<sub>2</sub> and MV lamp; ◇: TiO<sub>2</sub> and LEDs; ■: ZnO and MV lamp; □: ZnO and LEDs

The comparison was also performed on the basis of the electrical energy consumption to treat a unit volume ( $1.0 \text{ dm}^3$ ) suspension. Similar to the initial reaction rates, using MV lamp is more cost-effective compared to the LEDs, except for SMP using TiO<sub>2</sub>. In this case, TOC decrease was comparable to using MV lamp (Fig. 3).



**Figure 3.** The relative TOC values vs. the electrical energy input

●: MV lamp (no photocatalyst); ◆: TiO<sub>2</sub> and MV lamp; ◇: TiO<sub>2</sub> and LEDs; ■: ZnO and MV lamp; □: ZnO and LEDs

## Conclusions

The transformation of SMP and SMT can be performed effectively using both TiO<sub>2</sub> and ZnO photocatalysts, using MV lamp (300-400 nm) and LEDs (398 nm). The apparent quantum yields of the transformation were calculated and compared. It was found to be higher in the case of 300-400 nm radiation than in the case of 398 nm. The electric energy consumption of the MV lamps was significantly lower during the transformation of the sulfonamides, except for SMP. Similar tendencies can be seen for the complete removal of organic content. The behavior of SMP in the presence of TiO<sub>2</sub> irradiated with LEDs is very interesting and needs further investigation.

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